

Synthesis, structure and bonding of cadmium(II) thiocyanate systems featuring nitrogen based ligands of different denticity

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Abstract

Complexes catena-[di(4-amino-pyridine)di(μ -S,N-thiocyanato)cadmium(II)], $^1_\infty[\text{Cd}(\mu\text{-SCN})_2(\text{L}^1)]_2$ (**1**), catena-[(1-pyridine-2-yl-ethylene)-hydrazine]di(μ -S,N-thiocyanato)cadmium(II), $^1_\infty[\text{Cd}(\mu\text{-SCN})_2(\text{L}^2)]$ (**2**), and di- μ -S,N-thiocyanatobis{(N,N-diethyl-N'-(1-pyridine-2-yl-ethylidene)-ethane-1,2-diamine)(N-thiocyanato)cadmium(II)}, $[\text{Cd}(\text{NCS})(\mu\text{-SCN})(\text{L}^3)]_2$ (**3**) have been synthesized by reacting cadmium acetate/ NH_4SCN with 4-amino-pyridine (L^1), $\text{C}_5\text{H}_4\text{N}-\text{C}(\text{CH}_3)=\text{NNH}_2$ (L^2), and $\text{C}_5\text{H}_4\text{N}-\text{C}(\text{CH}_3)=\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{C}_2\text{H}_5)_2$ (L^3), respectively, in methanol. Characterization by single-crystal X-ray crystallography shows that in compounds **1** and **2** the cadmium atoms have a 4N2S-hexa-coordination sphere, exhibiting pseudo-octahedral geometry. The cadmium atoms are bridged by two thiocyanate ions generating 1-D polymeric chains. Compound **3** is a centrosymmetric dimeric complex, with the cadmium atom pseudo octahedrally surrounded by a 5N1S coordination sphere. In compound **1** the crystal packing is controlled mainly by interchain N–H \cdots N and C–H \cdots π interactions between the aminopyridine moieties, whereas in complexes **2** and **3** π -stacking interactions between the pyridyl planes stabilize the interchain or intermolecular packing, respectively. Thiocyanate and pyridylimine chelation to metal center is also scrutinized with EHMO analysis.

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Keywords: Cadmium(II); Thiocyanate; Schiff bases; Bonding; Coordination polymers

1. Introduction

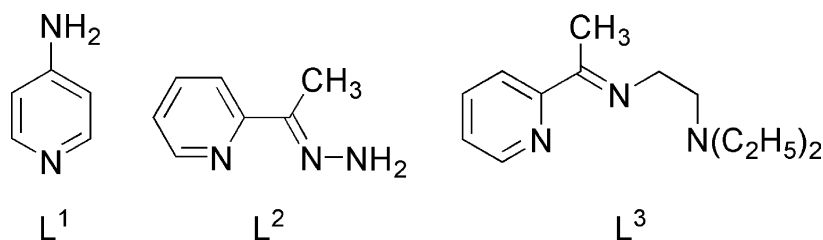
Metal–organic frameworks are widely regarded as promising materials for application in catalysis, separation and molecular recognition [1–4]. In construction of one/two/three dimensional frameworks, multidentate ligands are usually used to bridge metal centers to form polymeric structures. For instance, metal–organic coordination frameworks based on polycarboxylic acid, 4-4'bipyridine and thiocyanates have extensively been

studied [5,6]. Coordination polymers of cadmium, with pyridine-type ligands, are also investigated for their fluorescence properties [1,2,7]. Supramolecular contacts such as hydrogen bonding are frequently used as a powerful crystal engineering tool to “control” the packing of the molecular or extended building blocks [8–12]. In addition, π -interactions also offer the propensity for packing control in the solid crystalline state. Aromatic moieties which often occur as part of the organic ligands may either associate via displaced face-to-face π - π [13–17] or edge to face C–H \cdots π interactions [18–20].

Cadmium thiocyanate adducts of organic ligands are an important class of compounds for the design and preparation of such functional coordination frameworks,

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Scheme 1.

where Cd(II) forms stable double SCN bridged chains which are usually oriented along one direction [21]. In most cases, monodentate organic ligands, e.g., methyl-substituted pyridines, benzylamine, dibenzylamine, triphenylamine, 1H-1,2,4-triazole, imidazole, etc., were chosen and they occupy the remaining two trans coordination sites [22]. The steric and electronic effects of the monodentate ligands are found to be capable of modifying the chain structure [22]. With monodentate ligands capable of forming additional H-bonds, the chain structure has been extended to higher dimensional hydrogen bonded architectures [23]. On the other hand, propagation of the cadmium thiocyanate chain in the presence of bidentate or tridentate chelating ligands is not well documented [21g].

We report here the synthesis and crystal structure of three Cd(II) thiocyanate complexes with a monodentate ligand, 4-aminopyridine (L^1), a bidentate ligand, $C_5H_4N-C(CH_3)=NNH_2$ (L^2), and a tridentate ligand, $C_5H_4N-C(CH_3)=NCH_2CH_2-N(C_2H_5)_2$ (L^3) (Scheme 1). The ligands were chosen in such a way that they could undergo π - π alignment along with inter-chain H-bonding. The complex with L^3 represents a very rare example of a dimeric species in which Cd atoms are doubly bridged by two NCS ligands.

2. Experimental

2.1. Materials and physical measurements

Commercially available solvents such as 4-aminopyridine, hydrazine monohydrate, 2-acetyl-pyridine, *N,N*-diethylethylenediamine, cadmium acetate dihydrate and ammonium thiocyanate were used without further purification. Elemental analyses were carried out using a Perkin–Elmer 240C elemental analyzer. IR spectra were recorded in KBr (4500 – 500 cm^{-1}) using a Perkin–Elmer R XI FT-IR spectrophotometer.

2.2. Preparation of ligands

2.2.1. Synthesis of (1-pyridine-2-yl-ethylidene)-hydrazine (ligand L^2)

Hydrazine hydrate (85% aqueous, 0.75 g, 15 mmol) and 2-acetyl-pyridine (1.815 g, 15 mmol) were mixed in

methanol (20 ml) and then refluxed for 3 h. The resulting solution was evaporated to 5 ml and cooled to room temperature. Upon cooling the solution, a yellow solid precipitated, was collected by filtration and dried in vacuum over fused $CaCl_2$. Yield: 1.822 g (90%). (Found: C, 62.20; H, 6.62; N, 31.08%. Calc. for $C_7H_9N_3$: C, 62.22; H, 6.66; N, 31.11.) IR (ν/cm^{-1}): 3345–3285 (ν_{NH_2}), 1640 ($\nu_{C=N}$), 1590 (δ_{N-H}), 1447–1302 ($\nu_{\text{Pyridine ring}}$).

2.2.2. Synthesis of *N,N*-diethyl-*N'*-(1-pyridin-2-yl-ethylidene)-ethane-1,2-diamine (ligand L^3)

This ligand was prepared by a procedure similar to that for L^2 , by starting with *N,N*-diethylethylenediamine (1.74 g, 15 mmol) and 2-acetyl-pyridine (1.815 g, 15 mmol) to obtain a yellow liquid. Light yellow microcrystals were obtained by recrystallization from *n*-hexane. Yield: 2.792 g (85%). (Found: C, 71.20; H, 9.55; N, 19.22%. Calc. for $C_{13}H_{21}N_3$: C, 71.23; H, 9.58; N, 19.17.) IR (ν/cm^{-1}): 1648 ($\nu_{C=N}$).

2.3. Synthesis of metal complexes

2.3.1. $Cd(\mu-SCN)_2(4-H_2N-C_5H_4N_2)_\infty$ (1)

To a methanol solution (5 ml) of $Cd(OAc)_2 \cdot 2H_2O$ (0.53 g, 2 mmol) was added a methanol solution (10 ml) of NH_4SCN (0.30 g, 4 mmol). The solution was stirred for 10 min and the resultant colorless solution was then added to 15 ml of 4-amino-pyridine (L^1) solution (0.188 g, 2 mmol). The filtrate was allowed to stand in air at room temperature for 24 h, yielding colorless crystals. Yield: 0.388 g (95%). (Found: C, 34.54; H, 2.87; N, 20.15%. Calc. for $C_6H_6Cd_{0.50}N_3S$: C, 34.58; H, 2.88; N, 20.17.) IR (ν/cm^{-1}): 3297–3390 (ν_{NH_2}), 2076 (ν_{SCN}).

2.3.2. $Cd(\mu-SCN)_2\{2-C_5H_4N-C(CH_3)=NNH_2\}_\infty$ (2)

$Cd(OAc)_2 \cdot 2H_2O$ (1.33 g, 5 mmol) dissolved in methanol (20 ml) was added to a methanolic solution (10 ml) of NH_4SCN (0.76 g, 10 mmol) followed by ligand L^2 (0.34 g, 2.5 mmol) dissolved in (10 ml) methanol. The mixture was stirred for few minutes and dried in vacuo. Colorless crystals suitable for X-ray diffraction were obtained by dissolving the precipitate in hot DMSO and avoiding light for 24 h. Yield: 1.545 g (85%). (Found: C, 29.70; H, 2.45; N, 19.26%. Calc. for $C_9H_9CdN_5S_2$: C, 29.71; H, 2.47; N, 19.26.) IR (ν/cm^{-1}): 3290–3340 (ν_{NH_2}), 2096 (ν_{SCN}), 1596 ($\nu_{C=N}$).

2.3.3. $Cd(NCS)(\mu-SCN)\{2-C_5H_4N-C(CH_3)=N-(CH_2)_2N(C_2H_5)_2\}_2$ (**3**)

A methanolic solution of $Cd(OAc)_2 \cdot 2H_2O$ (0.53 g, 2 mmol) and NH_4SCN (0.30 g, 4 mmol) was added to a hot methanolic solution (10 ml) of ligand **L**³ (0.438 g, 2 mmol) with stirring. The resulting solution was allowed to stand at room temperature for two days to yield colorless crystals. Yield: 1.558 g (87%). (Found: C, 20.09; H, 2.33; N, 7.82%. Calc. for $C_{30}H_{42}Cd_2N_{10}S_4$: C, 20.11; H, 2.34; N, 7.82.) IR (ν/cm^{-1}): 2121 ($\nu_{\text{Bridging SCN}}$), 2044 ($\nu_{\text{Nitrogen bonded SCN}}$), 1655 ($\nu_{C=N}$).

2.4. Crystallographic studies

Diffraction data were collected at $T = 233(2)$ K (-40 °C) for **1** and **2** and at $T = 293(2)$ K (20 °C) for **3** by the ω -scan method with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and the use of a graphite monochromator on a Bruker Smart CCD. Data collection and cell refinement were done with SMART [24], data reduction with SAINT [24]. An experimental absorption correction was performed with SADABS [25]. The structure was solved by direct methods (SHELXS-97) [26]; refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite [26]. All non-hydrogen positions were found and refined with anisotropic temperature factors. In **1–3**, the hydrogen atoms were calculated with appropriate riding models (AFIX 43 for aromatic hydrogens on pyridine; AFIX 93 for NH_2 , AFIX 23 for CH_2 , AFIX 33 for CH_3) and $U_{eq}(H) = 1.2$ $U_{eq}(C, N)$ for CH and CH_2/NH_2 and $U_{eq}(H) = 1.5$ $U_{eq}(C)$ for CH_3 . In **2**, the largest difference peak (1.265 Å³) is around the Cd atom (0.814 Å). In **3**, the six strongest

peaks of the residual electron density are in the near vicinity (within 1.56 Å) of the cadmium atom. Graphics were computed with ORTEP3 for Windows [27]. Supramolecular interactions (hydrogen bonds, $C-H \cdots \pi$ contacts) were calculated with PLATON for windows [28–30]. Crystal data are listed in Table 1.

3. Results and discussion

The compounds $^1_{\infty}[Cd(\mu-SCN)_2(L^1)_2]$ (**1**), $^1_{\infty}[Cd(\mu-SCN)_2(L^2)]$ (**2**), and $[Cd(NCS)(\mu-SCN)(L^3)]_2$ (**3**) have been synthesized by reacting a methanol solution of $Cd(OAc)_2 \cdot 2H_2O/NH_4SCN$ with the respective ligand. Crystals were obtained in high yield ($>85\%$) either by solvent evaporation within two days (**1**, **3**) or from hot DMSO (**2**).

3.1. Crystal structures

The structure of compound **1** consists of doubly SCN-bridged 1-dimensional chains along the crystallographic b -direction with terminal 4-aminopyridine groups (Fig. 1). Each cadmium atom, which sits on a center of inversion, is pseudo-octahedrally coordinated by two *trans*-arranged sulfur atoms and two *trans*-arranged nitrogen atoms from the bridging thiocyanate groups. Two *trans*-coordinated 4-aminopyridine ligands complete the sixfold coordination geometry around cadmium. The double-bridging action of SCN gives rise to eight-membered $Cd_2(SCN)_2$ rings in a chair conformation because of the almost linear SCN group ($S-C-N = 178.9(3)^\circ$). The centroid of the $Cd_2(SCN)_2$ rings is

Table 1
Crystal data and structure refinement for the structures

Compound	1	2	3
Empirical formula	$C_6H_6Cd_{0.5}N_3S$	$C_9H_9CdN_5S_2$	$C_{30}H_{42}Cd_2N_{10}S_4$
M	204.40	363.73	895.78
Crystal system	orthorhombic	monoclinic	triclinic
Space group	$Pbca$	$P2_1/c$	$P\bar{1}$
a (Å)	14.080(3)	9.905(2)	7.33(3)
b (Å)	5.6874(13)	10.063(2)	10.06(4)
c (Å)	18.666(4)	13.612(3)	13.82(5)
α (°)	90	90	73.26(6)
β (°)	90	101.774(4)	83.29(7)
γ (°)	90	90	74.87(6)
V (Å ³)	1494.8(6)	1328.3(6)	941(6)
Z	8	4	1
μ_{calc} ($mg\ m^{-3}$)	1.852	1.819	1.581
Collected reflections (R_{int})	10 154/0.0393	11 530/0.0446	5008/0.0536
Unique data/restraints/parameters	1854/0/97	3201/0/154	3644/0/208
Final R indices [$I > 2\sigma(I)$]			
R_1	0.0558	0.0780	0.0785
wR_2	0.0633	0.0874	0.0971
R indices (all data)			
R_1	0.0283	0.0411	0.0455
wR_2	0.0558	0.0772	0.0840

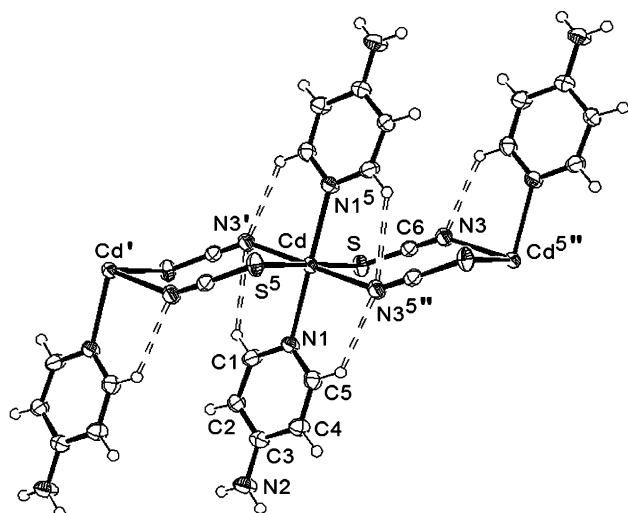


Fig. 1. Section of the one-dimensional chain of **1** with the intrachain C–H···N bonds; 50% thermal ellipsoids. Distances and angles are given in Table 2.

Table 2
Selected distances (Å) and angles (°) for **1**

Cd–N1	2.335 (2)
Cd–N3 ^{5''} /N3'	2.368 (3)
Cd–S	2.7565 (9)
S–C6	1.649 (3)
N3–C6	1.154 (3)
N1–Cd–N3'	91.18 (9)
N1–Cd–N3 ^{5''}	88.82 (9)
N1–Cd–S	91.60 (6)
N1–Cd–S ⁵	88.40 (6)
N3'–Cd–S	86.55 (6)
N3 ^{5''} –Cd–S	93.45 (6)

Symmetry transformations: ^l = $x, y - 1, z$; ⁵ = $-x + 1, -y, -z$; ^{5''} = $-x + 1, -y + 1, -z$.

a center of inversion. These chairs build up the 1-D chain through their corner-sharing action at the two cadmium atoms [22a,22b,22c,22d,31]. This type of *trans* oriented chain structure is usually found in most of the other Lewis-base adducts of Cd(II) thiocyanate [21b,22b,22c,32].

Weak intrachain C–H···N hydrogen bonds are formed from each pyridyl ring to the nitrogen donor atoms of the *cis*-coordinated NCS-ligands (Fig. 1, Table

Table 3
Hydrogen bonding interactions in **1**

Donor–H···acceptor	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
<i>Interchain</i>				
N2–H2B···N2 ⁷	0.87	2.56	3.434(4)	177.7
N2–H2C···N3 ⁸	0.87	2.45	3.232(4)	150.2
<i>Intrachain</i>				
C5–H5A···N3 ^{5''}	0.94	2.55	3.229(4)	129.8
C1–H1A···N3'	0.94	2.69	3.344(4)	127.3

Symmetry transformation: ^l = $x, y - 1, z$; ^{5''} = $-x + 1, -y + 1, -z$; ⁷ = $1/2 - x, -1/2 + y, z$; ⁸ = $x, 1/2 - y, -1/2 + z$.

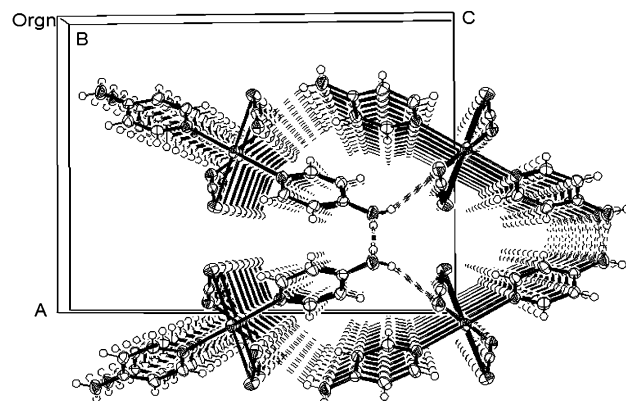


Fig. 2. Packing diagram with the interchain hydrogen bonding interactions in **1**.

3). The plane of the pyridyl ring is arranged along the *cisoid* N–Cd–N bonds with a slight deviation of 2.3° between the plane and the *cisoid* N–Cd–N bond axis. It is suggested that this close to coplanar/colinear arrangement is due to the C–H···N hydrogen bonding contributions [11,33]. While information on C–H···O bonding is plentiful, documentation of C–H···N bonds is scarce [11,34]. The interchain packing is controlled by weak interchain N–H···N hydrogen bonding between amino groups and from amino groups to the thiocyanato nitrogen atom (Fig. 2, Table 3) [35]. Furthermore, C–H··· π interactions [19,20] can be invoked between the pyridine moieties (Table 4).

In compound **2**, the structure consists of doubly SCN-bridged 1-dimensional coordination polymeric chains along the crystallographic *a*-direction with chelating (1-pyridin-2-yl-ethylidene)-hydrazine groups (Fig. 3). Each cadmium atom is pseudo-octahedrally coordinated by two *cis*-arranged sulfur atoms and four nitrogen atoms, two of which stem from the bridging thiocyanate groups. The two other nitrogen atoms come from the (1-pyridin-2-yl-ethylidene)-hydrazine ligand, giving rise to a five-membered chelate ring with the metal atom. As seen in compound **1**, the doubly bridging action of SCN gives rise to eight-membered Cd₂(SCN)₂ rings in a chair conformation because of the almost linear SCN group (S1–C8–N4 = 179.2(5)°, S2–C9–N5 = 176.4(4)°). Again, these chairs build up the 1-D chain through their corner-sharing action at the two cadmium atoms. Also, the centroid of the Cd₂(SCN)₂ rings is a center of inversion. Different from **1**, the S-bound thiocyanato groups are arranged in a *cis* fashion. This may be reasoned by a *trans*-influence so as to avoid competition for the π -bonding orbitals of the metal [36]. The propagation of doubly bridged thiocyanate chains in this manner, that is, with the *cis*-arrangement of the S-atoms, although preferred electronically, is not common with monodentate ligands, probably due to steric reasons. A notable exception [32] is *catena*-bis(2-methylpyridine)bis(μ -thiocyanato-N,S)cadmium(II) where both *cis* and *trans* orientations

Table 4
Aromatic–aromatic interactions in **1**

Cg(I)...Cg(J)	Cg–Cg	α	β	γ	CgI_perp	Cg.T_perp
Cg(I)–Cg(I) ⁴	5.133(2)	63.34	28.79	72.87	1.512	4.498
Cg(I)–Cg(I) ^{7'}	4.842(2)	65.50	8.48	68.14	1.803	4.789
C–H(I)...Cg(J)	H...Cg(Å)	perpend, contact H...ring plane (Å)		angle C–H to ring normal (°)	C–H...Cg (°)	
C2–H2A...Cg(I) ⁷	2.84	2.729		16.33	139.77	
C4–H4A...Cg(I) ^{4'}	3.29	3.236		10.23	133.02	

Cg(I), plane number I, here pyridyl ring; Cg–Cg, distance between ring centroids (Å); α , dihedral angle between planes I and J (°); β , angle Cg(I) → Cg(J) or Cg(i) → Me vector and normal to plane I (°); γ , angle Cg(I) → Cg(J) vector and normal to plane J (°); CgI_Perp, perpendicular distance of Cg(I) on ring J (Å); CgJ_Perp, perpendicular distance of Cg(J) on ring I (Å).

Symmetry transformation ⁴ = 1 – x, –1/2 + y, –1/2 – z; ^{4'} = 1 – x, 1/2 + y, –1/2 – z; ⁷ = 1/2 – x, –1/2 + y, z; ^{7'} = 1/2 – y, 1/2 + y, z.

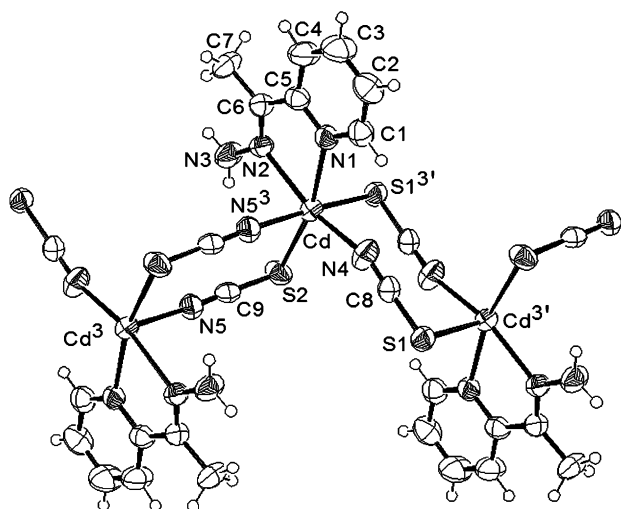


Fig. 3. Section of the one-dimensional chain of **2**; 50% thermal ellipsoids: symmetry transformation ³ = –x, –y + 1, –z; ^{3'} = –x – 1, –y + 1, –z. For distances and angles see Table 5.

appear alternatively in the chain [37]. It is suggestive that the bidentate chelating blocking ligands, which must occupy the two *cis*-coordination sites, may dictate the *cis*-arrangement of the S-atoms as was also found in catena-(*N,N,N',N'*-tetramethylethylenediamine)bis(μ -thi-

ocyanato-*N,S*cadmium (II), $[\text{Cd}(\mu\text{-SCN})_2(\text{Me}_2\text{NCH}_2\text{-CH}_2\text{NMe}_2)]$ [21g]. The propagation of the chain, i.e., relative orientation of the coordinating atoms in **2**, is, however, different from the reported structure of $[\text{Cd}(\mu\text{-SCN})_2(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)]$. In the latter, both S-atoms are *trans* to the N-atoms of the chelating ligand which gives rise to planar eight-membered $\text{Cd}_2(\text{SCN})_2$ rings. In **2**, one of the S-atoms is *trans* to the pyridyl N-atom and the other is *trans* to the N atom of a thiocyanate ion resulting in $\text{Cd}_2(\text{SCN})_2$ rings in the chair conformation.

The interchain packing in **2** along the *c*-direction is controlled by interchain N–H...N hydrogen bonding between one hydrogen of the amino group to the thiocyanato nitrogen atom (N3–H3A...N5²: H3A...N5² 2.61 Å, N3...N5² 3.345(6) Å, N3–H3A...N5² 142.5°, symmetry transformation ² = –x, –1/2 + y, –1/2 – z) [35]. Along the *b*-direction, there are very weak interchain π -stacking interactions between the pyridyl planes (Fig. 4) [16]. The only weakly overlapping pyridyl ring planes are related by a center of inversion, thus, are exactly parallel. The ring slippage is large with a slip angle of 31.9° or a vertical displacement between the ring centroids of 2.11 Å (centroid separation 3.98 Å, interplanar distance 3.38 Å) [16,17,33,35c,38,39]. The overlapping carbon contact C1–C2^{3''} is 3.385(8) Å.

Table 5
Selected distances (Å) and angles (°) for **2**

Cd–N1	2.329(4)	N1–Cd–N5 ³	89.41(13)
Cd–N2	2.380(4)	N4–Cd–N2	162.49(16)
Cd–N4	2.277(4)	N1–Cd–N2	69.43(13)
Cd–N5 ³	2.343(4)	N5 ³ –Cd–N2	88.25(14)
Cd–S1 ^{3'}	2.7645(13)	N4–Cd–S2	103.80(13)
Cd–S2	2.6526(14)	N1–Cd–S2	162.92(10)
N2–C6	1.275(6)	N5 ³ –Cd–S2	92.21(10)
N2–N3	1.363(5)	N2–Cd–S2	93.61(10)
S1–C8	1.646(5)	N4–Cd–S1 ³	94.31(11)
N4–C8	1.145(6)	N1–Cd–S1 ³	96.83(9)
S2–C9	1.650(5)	N5 ³ –Cd–S1 ³	172.61(10)
N5–C9	1.44(5)	N2–Cd–S1 ³	90.22(10)
N4–Cd–N1	93.22(15)	S2–Cd–S1	80.66(4)
N4–Cd–N5 ³	89.28(15)		

Symmetry transformations: ³ = –x, –y + 1, –z; ^{3'} = –x – 1, –y + 1, –z.

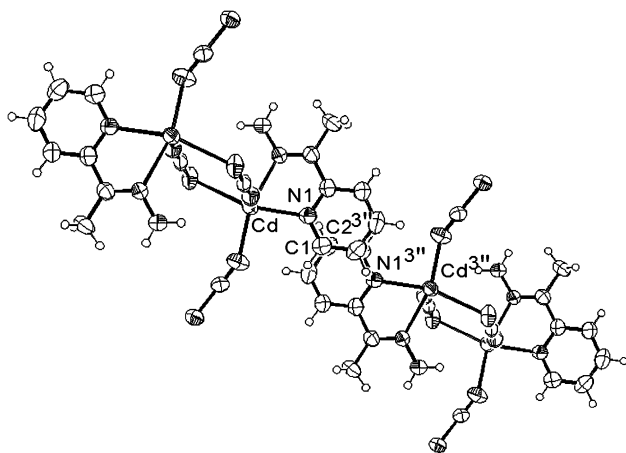


Fig. 4. Weak interchain π -stacking along b in **2**; symmetry transformation $3^m = -x-1, -y, -z$.

Compound **3** is a dimeric complex with the tridentate chelating *N,N*-diethyl-*N'*-(1-pyridin-2-yl-ethylidene)-ethane-1,2-diamine ligand (L^3), one terminal (N-bound) thiocyanato group and two bridging thiocyanato ligands around cadmium. Thus, each cadmium atom is pseudo-octahedrally coordinated by five nitrogen donors and a sulfur atom. The terminal and bridging thiocyanato groups are arranged *trans* to each other (Fig. 5). The two halves of the dimer are related by a center of inversion as the centroid of the $\text{Cd}_2(\text{SCN})_2$ rings. No disorder in the NCS versus SCN binding, both for the terminal or bridging thiocyanato ligands, was apparent from the structure refinement. The N and S atoms could be assigned without ambiguity. It is to be noted that only one dimeric $\text{Cd}_2(\mu\text{-SCN})_2$ structure in cadmium(II) thiocyanate adducts has been reported to date. To the best of our knowledge, all the other structures with the $\text{Cd}_2(\mu\text{-SCN})_2$ fragment being polymers [32]. This other example, bis(μ -thiocyanato)-(μ -1,4,7,16,19,22-hexa-aza-10,13,25,28-tetraoxacyclotriacontane)-dibromo-dicad-

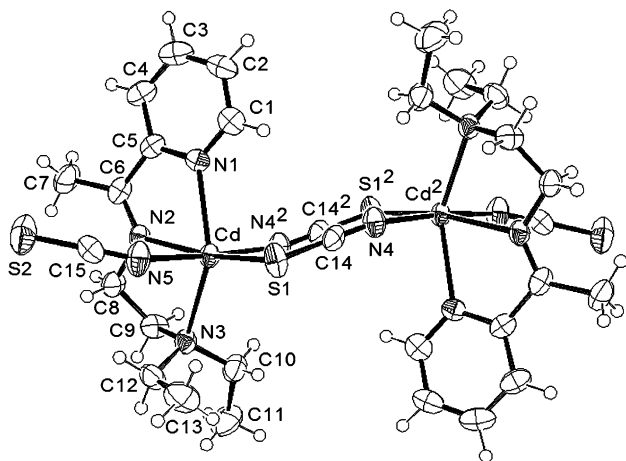


Fig. 5. Molecular structure of **3**; 50% thermal ellipsoids: $3 = -x, -y+1, -z$; $3' = -x-1, -y+1, -z$.

mium(II), involves the use of an aza-crown macrocycle which surrounds the whole $\text{Cd}_2(\mu\text{-SCN})_2$ entity, thus, preventing formation of an extended structure. The aza-crown ligand employs three meridional coordination sites at cadmium [40].

The tridentate ligand, L^3 , in compound **3** also leaves only three coordination sites to be occupied by two bridging and one terminal thiocyanate ions. The doubly bridged dimer is, however, preferred to other possible structures, e.g., singly bridged polymeric chain with coordination number six or doubly bridged polymeric chain with coordination number seven (see Table 6).

The intermolecular packing is controlled by typical π -stacking interactions between the pyridyl planes (Fig. 6) [16,17,33,35c,38,39]. The overlapping ring planes stack in an ...ABC... fashion and are related by a center of inversion, thus are exactly parallel. The ring slippage is typical with a slip angle of 22.0° (N1/un-primed to N1^{2m}/double-primed ring) or 25.2° (N1/un-primed to N1^{2'}/single-primed) ring. This corresponds to a vertical displacement between the ring centroids of 1.34 or 1.61 Å, respectively (centroid separation 3.576 or 3.785 Å, interplanar distance 3.32 or 3.43 Å, respectively) [15b,21–23]. The shortest and overlapping carbon contacts are $\text{C1-C3}^{2''} = 3.32(2)$ Å and $\text{C5-C3}^{2'} = 3.49(2)$ Å, respectively.

3.2. Bonding analysis

With the aim to investigate the nature of bonding in the polymeric complex **1**, we would like to consider a repetitive molecular motif in which the metal is coordinated to two *trans* 4-aminopyridine ligands along with two isothiocyanate and two thiocyanate bridging coligands in a mutually *cis* geometry. This arrangement is not suited for maximizing the back bonding effect, but the choice of the molecular fragment is unique to avoid any unwanted steric encumbrance between large sulfur atoms in basal plane. In fact, the

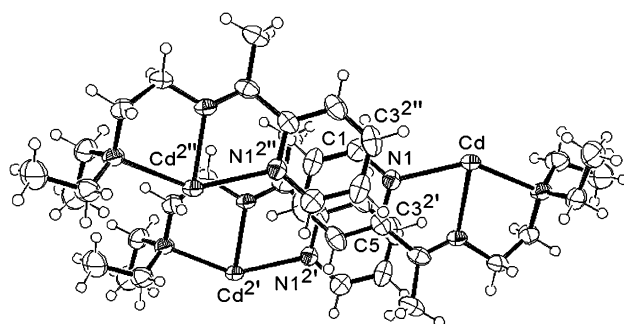


Fig. 6. Intermolecular π -stacking in **3** in an ABCB fashion; the SCN groups are omitted and only the asymmetric half of the dimeric molecule is shown for clarity. Top-view of the π -overlap between the ABC molecules to show the typical ring slippage; symmetry transformation $2' = -x+1, -y+1, -z+1$; $2'' = -x, -y+1, -z+1$.

Table 6
Selected distances (Å) and angles (°) for **3**

Cd–N1	2.419(8)	N2–Cd–N1	68.0(3)
Cd–N2	2.322(9)	N5–Cd–N1	91.9(3)
Cd–N3	2.421(8)	N4 ² –Cd–N3	91.9(3)
Cd–N4 ²	2.314(8)	N2–Cd–N3	75.9(2)
Cd–N5	2.350(9)	N5–Cd–N3	93.7(3)
Cd–S1	2.616(8)	N1–Cd–N3	142.6(2)
N4–C14	1.164(8)	N4 ² –Cd–S1	92.4(3)
N5–C15	1.151(8)	N2–Cd–S1	163.09(14)
C14–S1	1.627(8)	N5–Cd–S1	82.8(3)
C15–S2	1.631(8)	N1–Cd–S1	102.5(3)
N4 ² –Cd–N2	100.5(3)	N3–Cd–S1	114.9(2)
N4 ² –Cd–N5	173.73(19)	N4–C14–S1	179.2(6)
N2–Cd–N5	83.6(3)	N5–C15–S2	178.5(7)
N4 ² –Cd–N1	85.3(3)		

Symmetry transformations: ² = $-x + 1, -y, -z + 1$.

trans orientation of bulky S atoms relaxes the steric constraints which can be quantitatively measured with the angular parameters α and β of the ambidentate ligands.

The LUMO ($E = -11.790$ eV) constitutes of conjugated $2p\pi^*$ framework of *trans* pyridyl moieties almost in an exclusive ($\sim 95\%$) manner. The portrayal of bonding sequences has led us to comprehend that the consecutive MOs experience better stabilization with low energy conjugated π^* molecular orbitals of pyridyl group rather than utilizing high energy localized π^* set of ambidentate ligands. The HOMO ($E = -11.949$ eV) primarily resides ($\sim 85\%$) over the π -conjugated sp^2 hybrid orbitals of 4-aminopyridyl ligands, which in turn are nearly perpendicular to $p\pi^*$ framework of LUMO. The lowest energy MO utilizes the pyridyl nitrogen σ -orbitals, logically due to pronounced electron-releasing effect (+R) of *para* amino group. The small HOMO–LUMO gap (~ 0.16 eV) of the concerned molecular unit provides opportunity of internal mixing to reshuffle their energy accordingly and adjust the electronic perturbations in forming the extended molecular network.

Bonding in complex **2** can similarly be rationalized with the concept of taking a molecular motif, which symmetrically propagates to form a polymeric network. The metal in the octahedral molecular motif is coordinated through one of each thiocyanate and isothiocyanate groups in a mutual *trans* manner. Angle subtended by the pyridylimine ligand with the metal in equatorial plane is 69.4° , providing large vacant space to accommodate the remaining NCS and SCN groups in a *cis* geometry with a relaxed intermediate angle of 103.8° . This particular arrangement of donor atoms in coordination sphere is simultaneously favored by both steric and electronic factors. Steric relaxation in basal plane directly influences the specific arrangement of bridging ambidentate coligands to enjoy appreciable back-bonding stabilization.

The mostly antibonding MO exclusively shares the σ^* orbitals (out of phase) of NCS ligands. Next to this,

the consecutive antibonding MOs share the π^* orbitals of NCS moiety. On decreasing energy, MOs spread mostly over the π^* framework of $=N=NH_2$ moiety. The N–NH₂ fragment possesses considerable double bond character as evident from observed N–N distance (1.363 Å), intermediate of N,N single bond (1.45 Å) and double bond (1.25 Å) length. The LUMO ($E = -11.769$ eV) is stabilized over the extended $p\pi^*$ network ($\sim 90\%$) of pyridylimine schiff-base ligand. This observation is logical from electronic viewpoint. π^* orbital of imine (C=N) functionality undergoes symmetry allowed overlap with energetically compatible $\pi_{N=N}$ orbital leading to a conjugated low energy π^* acceptor orbital. HOMO is situated entirely ($\sim 95\%$) on conjugated symmetrical $p\pi$ bonding MOs. The in-phase conjugated $\pi_{N=N}$ set share $\sim 25\%$ of HOMO. From the above discussion, it is clear that the orbital interactions in HOMO and LUMO primarily originate from participation of π and π^* molecular orbital sets of conjugated C–N–N fragment. In contrast to complex **1**, here all the interactions mostly care imine nitrogen (polarizable π set) rather than the pyridyl nitrogen presumably due to N–NH₂ conjugation. The small HOMO–LUMO gap (~ 0.12 eV) allows the electronic redistribution in frontier orbitals of extended lattice, like in **1**.

The complex **3** possesses plane of symmetry and it is justified to consider the asymmetric unit (half of the total molecule) for our present investigation. The MO of highest energy is localized exclusively ($\sim 95\%$) over the σ^* framework of the NCS group, whereas the extremely stable MO encompasses the σ bonding electron density ($\sim 85\%$) of unsaturated five membered pyridylimine chelate moiety. The HOMO ($E = -11.604$ eV) primarily resides over the p type bonding orbitals of dimethylene bridged puckered chelate ring and also on the two dangling ethyl groups. The LUMO ($E = -11.278$ eV) is mainly concentrated ($\sim 70\%$) on the nearly antibonding molecular orbitals of saturated five membered metallo-ring. The contribution of pendant ethyl groups towards LUMO is significantly less (by $\sim 45\%$) than what is

observed for HOMO. Antibonding acceptor orbitals of the ethyl groups are too high in energy to undergo symmetry allowed in-phase interaction with that of saturated metallo-ring. Both the HOMO and LUMO are stabilized by direct involvement of Schiff-base ligand orbitals. The pyridyl nitrogen has no significant contribution towards HOMO and LUMO, whereas imine and tertiary amino nitrogen orbitals are appreciably engaged in stabilization of those frontier MOs. The reason possibly stems from the marked difference in basicity of the N-donor sites ($N^{\text{pyridyl}} < N^{\text{imine}} \ll N^{\text{amino}}$). The splitting of metal 4d orbitals will be small and will not be energetically suitable to interact with ligand group orbitals. Hence, the metal orbitals have no contribution in either HOMO or LUMO. Considerably high HOMO–LUMO energy gap (~ 0.33 eV) renders the complex less polarizable and reluctant to participate in any electron transfer events compared to **1** and **2**.

The Extended Huckel calculations were performed on all three complexes using CACAO package developed by Mealli and Proserpio [41].

4. Conclusions

We have isolated three cadmium(II) complexes of thiocyanate, ranging from polymeric to dimeric molecular products by varying the denticity of nitrogen containing ligands. Both the monodentate and bidentate ligands, L^1 and L^2 , yield doubly bridged thiocyanate chains. The relative orientation of atoms around Cd(II) is, however, different in the two structures; the two *trans*-arranged sulfur atoms in the former and two *cis*-arranged sulfur atoms in the latter. The tridentate ligand L^3 , on the other hand, results in a very unusual dimeric complex. The interchain packing in **1** and **2** is controlled by the N–H...N hydrogen bonding between the hydrogen of amino groups and the thiocyanate nitrogen atoms along with weak secondary non-covalent interactions. In complex **3**, the intermolecular packing is controlled by typical π -stacking interactions between the pyridyl planes.

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Appendix A. Supplementary material

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre as Supple-

mentary Publication Nos. CCDC – 216945 (Compound **1**), – 216946 (compound **2**), – 216948 (compound **3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2004.07.048.

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